

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(21) Application number: 86905404.9 (51) Int. Cl.³: C 04 B 35/10

(22) Date of filing: 04.09.86

Data of the international application taken as a basis:

(60) International application number:
PCT/JP86/00449

(61) International publication number:
WO87/01369 (12.03.87 87/06)

(30) Priority: 06.09.85 JP 197155/85
24.09.85 JP 210710/85

(40) Date of publication of application:
16.09.87 Bulletin 87/38

(62) Designated Contracting States:
DE FR GB

(71) Applicant: NIPPON SODA CO., LTD.
2-1, Ohtemachi 2-chome
Chiyoda-ku Tokyo, 100(JP)

(72) Inventor: KIMURA, Nobuo
680, Takeda Odawara-shi
Kanagawa 250-02(JP)

(72) Inventor: OKAMURA, Hiromichi
3-14-13, Ougi-cho Odawara-shi
Kanagawa 250(JP)

(72) Inventor: MORISHITA, Junichi
316, Nakazone Odawara-shi
Kanagawa 250(JP)

(74) Representative: van der Beek, George Frans et al,
Nederlandsch Octrooibureau Johan de Wittlaan 15 P.O.
Box 29720
NL-2502 LS 's-Gravenhage(NL)

(54) **HIGH-DENSITY ALUMINA-ZIRCONIA SINTER AND PROCESS FRO ITS PRODUCTION.**

(57) A high-density alumina-zirconia sinter, which comprises more than 60 mol % to 99 mol % of α -alumina, 1 mol % to less than 40 mol % of zirconia containing at least 65 % of a tetragonal crystal phase, and a transition metal oxide in an amount of 0.01-1% in terms of an atomic ratio of a transition metal to the sum of aluminum and zirconium, and which has a remarkably high sintering density, high strength, high toughness, and high hardness useful as mechanical members, abrasion-resistant materials, cutting tools, etc. This sinter can be obtained by dispersing α -alumina powder or its precursor powder and zirconia powder or its precursor in a solution or suspension of a transition metal compound, and sintering the powder obtained from the resulting dispersion. Particularly preferable starting powders include alumina-zirconia composite powder obtained by mixing a dispersion of α -alumina powder in an aqueous solution of a zirconium salt with a precipitating agent, and calcining the obtained composite powder.

EP 0 236 507 A1

BEST AVAILABLE COPY

Title of Invention

HIGH DENSITY ALUMINA ZIRCONIA CERAMICS AND A PROCESS FOR PRODUCTION
THEREOF

Technical Field

5

The present invention relates to high density alumina zirconia ceramics consisting essentially of alumina and zirconia, and further to the method of the production thereof.

The high density alumina -zirconia ceramics of the present invention 10 is highly hard and abrasion highly resistant and has high toughness, and therefore, can be expected to have a variety of applications such as for a mechanical member, abrasion resistant material, and tooling material.

Background Art

15

Alumina ceramic material is famous one in use for cutting tool ceramics, and has high abrasion resistance, but is disadvantageous in easy pitching. Therefore, the improvement of toughness is a major object of development of the alumina ceramics.

20 One known way of improving the toughness of alumina ceramics is that zirconia phases are finely dispersed in the alumina matrix so that the finely dispersed tetragonal zirconia phase can transform to monoclinic phase under the stress field at the end of crack to transfer, and therefore the energy of crack transfer in the alumina ceramics 25 will be absorbed. When zirconia phase does not contain a stabilizing agent, zirconia particle will maintain to be tetragonal and stable in the

alumina matrix. The size of the particle needs to be less than the critical size (in order of $0.5 \mu\text{m}$). However, such fine dispersion can not be produced in commercial size for the production of the ceramic body. One was proposed in Japanese Patent Laid Open Gazette No.54-25908

5 for the production of so fine dispersion wherein partially stabilized zirconia is added to the ceramic formulation so as to maintain tetragonal even when the size of zirconia is more than the critical particle size.

In order to yield high density ceramics with fine dispersion of zirconia in the ceramics, the higher temperature sintering such as 10 at the temperature higher than 1500°C under the atmospheric pressure, ordinarily the sintering temperature of higher than 1600°C is necessary. When the lower sintering temperature is used for producing the high density ceramics, the higher pressure for sintering should be applied (HIP treatment). However, the sintering under higher pressure is not 15 preferable and further, when the ceramics is sintered at the higher temperature under the atmospheric pressure, the grain growth of alumina and the grain growth of zirconia together with the transformation of the crystal to monoclinic phase may easily occur so as to decrease the strengthening with zirconia.

20 In accordance with the present invention, the sintering ability of the ceramics is improved by the combination of alumina phase and zirconia phase, so that the grain growth of alumina and zirconia would be suppressed to result in the high density alumina zirconia ceramics with high breaking toughness and high abrasion resistance.

25 The inventive alumina zirconia ceramics is a functional ceramics having high strength and high tenacity, and it is expected to use for structural material such as mechanical material, abrasion resistant material, and cutting material and etc..

It is one object of the present invention to produce the dense 30 ceramics having high density and controlled microstructure by suppressing

the grain growth in the ceramics to have objective functions, for example, in the alumina zirconia ceramics, oxygen ion conductivity, thermal stability, mechanical properties and the like, and the inventive alumina zirconia ceramics has such objective functions as mechanical properties such as bending strength, tenacity and the like.

There has been produced dense alumina zirconia ceramics having controlled microstructure by special moulding technique, and high pressure sintering technique such as hot press technique or HIP method. However, these methods need complicated operation and special installations, and therefore, the resultant product will be entirely expensive.

On the other hand, there has been proposed a process for the production of ceramics which comprises preparing the raw material powder by using chemical technique such as co-precipitation or the like and then sintering a moulding of the obtained raw material powder at the relatively low temperature range.

However, it is known that in general the more finely divided particulate material has the stronger cohesive force. Therefore, it is difficult to produce ceramics having high density with high reproducibility from the chemically treated raw powder.

Further, there has been proposed the addition of sintering activator, for example, Japanese Laid open Gazette No. shou 5010351 describes a process for the production of ceramics comprising moulding and sintering a raw material powder which is obtained by adding aqueous ammonium to the mixed aqueous solution containing water soluble zirconium salt, water soluble salts of calcium, magnesium, yttrium and the like as a stabilizing agent(s), and water soluble salt of the transition metal for sintering activator, so as to precipitate the desired co-precipitated hydroxide containing the desired metals, then, drying and calcining thereof. The raw material powder can not provide satisfactory lower temperature sintering characteristics nor enough relative density of the ceramics.

In the above mentioned process, aqueous ammonium is used for precipitation. Some of transition metals will form amine complex with ammonium so that in practice aqueous ammonium can not be used in cases of such transition metal.

5 In order to avoid this shortcoming, there is a process in that the oxides of the transition metals are used in place of the water soluble salt of the transition metals so as to disperse in the the mixed solution containing the other components whereas the hydroxides of the other metal components are coprecipitated together with oxides of the transition
10 metals.

F. F. Lange reported in Journal of Materials Science 17, 250-256(1982) that "There is critical limit of the particle size of tetragonal phase respectively to Y_2O_3 content, and when the size exceeds the critical limit, the tetragonal phase can not be present. Though the critical particle 15 size is more than 1 μm at the Y_2O_3 content of 3 mol. %, it decreases to in order of 0.2 μm at the content of 2 molar %."

However, the suppressing of the growth of crystal grain in the ceramics, to control the size of the crystal grain to in order of equal to or less than 0.2 μm is extremely difficult by the prior art process for
20 the production of the ceramics.

The characteristics of sintering at the lower temperature such that the grain size be controlled approximate 0.2 μm or less cannot be attained even by using the raw material powder prepared by the co precipitation.

25 As described above, the known alumina zirconia ceramic material is not satisfactory in view of improving the mechanical strength and stability, and therefore, ceramics with higher tenacity and strength has been highly desired.

30 It is the object of the present invention to provide a process for

0236507

the production of the raw material powder with characteristics of
sintering at the lower temperature, which can be used for the production
of the dense alumina zirconia ceramics as well as a process for the
production of the dense alumina zirconia ceramics with controlled crystal
structure.

0236507

It is another object of the invention to provide a method of the
production of alumina zirconia ceramics with high fracture tenacity which
comprise sintering at relatively lower temperature under the atmospheric
pressure the specified raw powder of alumina and zirconia.

Disclosure of Invention

The present invention comprises a high density alumina -zirconia ceramic body, the formulation of which comprises
5 α -alumina ranging from 60 mole % to 99 mole %, zirconia containing more than 65 % of tetragonal phase content ranging from 1 mole % to 40 mole % and transition metal oxide(s) the atomic ratio of which to the combination of aluminium and zirconium ranges 0.01 % to 1 %
10 for the production of high density alumina-zirconia ceramic, which comprises moulding and sintering the raw material powder prepared by the above mentioned process.

When the content of zirconia is less than 1 mole %, the high toughness of the resultant ceramics can not be obtained. Further, When the content 15 of zirconia exceeds 40 mole %, the hardness of the resulting ceramics will be decreased.

The high density alumina zirconia ceramic body of the present invention can be produced in accordance with the following method.

Zirconia powder having the grain size of less than 300 Å and BET 20 relative surface area of more than 8 m^2/g or the precursor to generate the zirconia powder by heat decomposition, and α -alumina powder having the grain size of less than 1.0 μm and the BET relative surface area of more than 5 m^2/g , or the precursor to generate 25 the α -alumina powder by heat decomposition are mixed in the solution or the dispersion containing compound(s) of at least one metal selected from the group consisting of Mn, Fe, Co, Ni, Cu, and Zn and then removing the solvent and drying to yield the combined powder. The resultant powder is moulded in a shape, and then fired under the room pressure at the temperature of lower than 1500 °C to sinter. The resultant sintered 30 ceramic body is obtained.

The stabilizing agent when used zirconia powder is a partially stabilized zirconia in this invention may be Y_2O_3 , CaO , MgO or CeO_2 , as well as yttrium compounds, calcium compounds, magnesium compounds, or cerium compounds to generate respectively Y_2O_3 , CaO , MgO , or CeO_2 , by its 5 thermal decomposition.

Ordinarily, Y_2O_3 is used as a stabilizing agent, and the amount to be added is less than 3 mole % in case of Y_2O_3 , and less than 12 mole % in case of MgO or CaO , and the amount to be added to the ceramics composition is less than 14 mole % in case of CeO_2 . If the content of the stabilizing 10 agent exceeds the above limits, the toughness of the resulting ceramics will be lowered. The used zirconia powder should have the grain size of less than 300 Å, and the BET specific surface area of more than $8 m^2/g$, which may be prepared by any process. Further any precursor to generate such powder of the above mentioned properties upon heat decomposition or 15 pyrolysis can be used in the present invention.

Any of α -alumina of the above mentioned properties to satisfy the above explained condition or the precursor to generate such α -alumina can be used without any special limitation.

In accordance with the present invention, the raw material is produced 20 as a combined deposit or co-precipitation of zirconium compound and alumina, from aqueous dispersion containing zirconium salt (or zirconium salt and a stabilizing agent) and alumina powder and precipitating agent, and then the deposit is calcined to prepare the combined powder of alumina and zirconia. This combined powder is 25 especially preferable for the production of the inventive ceramics.

In the concrete method of the raw material used for the inventive alumina zirconia ceramics, alumina powder is added to an aqueous solution of zirconium salt (or an aqueous solution of zirconium and stabilizing agent) to prepare the aqueous dispersion. Then, the resulting dispersion 30 is added to ammonia water and agitated and the precipitation is formed.

Alternatively, aqueous solution of zirconium salt (or aqueous solution of zirconium and stabilizing agent) is added to a dispersion of alumina powder and ammonia water, and agitated and then, the precipitation is formed to prepare the raw material for the production of the alumina zirconia ceramics of the present invention. The zirconium salt is soluble in water, and the regulation of the pH will produce the hydrated oxide. The resulting oxide may produce zirconia by calcining. Such salt may include oxychloride, oxynitrate, oxyacetate, oxysulfate and the like.

In the production of the ceramics, when the particle size of the raw material zirconia powder exceeds 300 Å, or when the BET specific surface of the zirconia powder is less than 8 m²/g, or when the particle size of the raw material α -alumina exceeds 1.0 μ m, or when the BET specific surface of the α -alumina is less than 5 m²/g, the high density of the resulting ceramics can not be obtained only by sintering at the temperature of below 1500 °C. In the other words, enough dense ceramics of high density can not be obtained by the atmospheric sintering at the lower temperature.

The atomic ratio of the transition metal to the combination of Al and Zr in the production of the ceramics may be in a range of from 0.01 % to 1.0 %, preferably 0.01 % to 0.5 %. If the ratio exceeds 1.0 %, the sintering properties are affected. And if the ratio is below 0.01%, enough dense ceramics of high density can not be obtained.

The transition metal compound(s) in this invention may be oxide of at least one metal selected from the group consisting of Mn, Fe, Co, Ni, Cu, and Zn as well as the compound(s) to generate one of the above mentioned metal oxide by its thermal decomposition. As the transition metal compound, there may be used inorganic compounds such as oxides, hydroxides, nitrates, chlorides and the like of the above mentioned metals: organic acid salts such as oxalates, acetates, propionates, higher fatty

acid salt and the like of the above mentioned metals:

0236507

and organic metal compounds such as alkoxide compounds, chelate compounds and the like of the metals, even if it is not only soluble but also insoluble to the used solvents. Preferable one is solvent soluble

5 compounds.

Removal and drying of solvent is carried out by the conventional evaporation method, but if the transition metal compound is not soluble in water nor organic solvent, or if the soluble compound is readily precipitated by using a precipitating agent, the filtration can be used 10 for removal of solvent. Further, a spray drying technique can be applied for effective and efficient production of volume raw powder.

While the combined powder obtained from the mixture of zirconia powder (or the precursor thereof), α -alumina powder (or the precursor thereof), and the transition metal compound can be used as a starting 15 material for the ceramics, the powder is preferably calcined at the temperature of 400 °C to 1000 °C particularly when the powder contains the precursor materials

The conventional moulding technique can be satisfactorily used to form the raw material in a shape, but preferably the hydrostatic 20 compression should be applied after moulding under the lower pressure so as to improve the sintered density and the mechanical strength of the final ceramic body.

The sintering of the moulding may be carried out by any of the conventional methods, and the ordinary sintering under the atmospheric 25 pressure can be satisfactory to produce the enough dense ceramics.

The ceramics obtained by the inventive method has zirconia grain size in average of less than 1.0 μ m, preferably less than 0.5 μ m and the content of tetragonal phase of more than 65 %, preferably more than 80 %. The average size of alumina grain in the ceramics is less than 3 μ m, 30 preferably 2 μ m or less.

As before mentioned, the improvement of the toughness and abrasion resistance of the alumina ceramics needs the uniform and fine dispersion of fine zirconia grains in the ceramics, but it needs high temperature sintering of the ceramics for obtaining the high density. If it is not sintered at the higher temperature, it will result in lowering of the hardness and toughness.

In accordance with the present invention, firing in the presence of the transition metal compound(s) including Mn, Fe, Co, Cu, Ni or Zn as a metal species will improve the sintering ability of the material to result in the excellent high density alumina zirconia ceramics.

The high density alumina zirconia ceramics of the present invention can maintain higher content of tetragonal phase, even when zirconia content is increased in the ceramics having the lower content of the stabilizing agent. Therefore, the resulting ceramics can have higher hardness and higher toughness. This fact indicates that the grains in the ceramics are suppressed, and therefore, the fine zirconia grains are well and uniformly dispersed.

The transition metal compound(s) can suppress the grains of zirconia and alumina from growing in the ceramics, so that the resulting ceramics will be densified. On the other hand, ZrO_2 grains well dispersed in Al_2O_3 phase will suppress the grains of Al_2O_3 growing as well as suppress the transformation of tetragonal phase to monoclinic phase. Therefore, the toughness of the resulting ceramics is significantly increased.

These phenomenon functions synergically so that the toughness, hardness and abrasion resistance of the resulting ceramics are significantly improved to have $12 \text{ MN/m}^{3/2}$ of K_{Ic} .

Best Mode for Carrying out the Invention

5 The best mode for carrying out the invention may be illustrated by the following examples. However, the following examples are not given for limitation of the scope of the invention.

EXAMPLE 1(1) Production of Raw Material Powder

10

The pH of the combined solution containing $ZrOCl_4$ and YCl_3 was regulated to co-precipitate the deposit of the combined hydroxides. The resultant co-precipitation was calcined to yield the partially stabilized zirconia having the content of Y_2O_3 as shown in Table 1, and 15 the characteristics of powder as shown in Table 1.

The resultant powder, α -alumina having the characteristics as shown in

Table 2, and the nitrate of the transition metal were dissolved in ethanol, and the resultant ethanolic solution is put in pot for milling, and mixed and ground and then ethanol was evaporated to dry thereby to yield the raw powder for the production of ceramic body which have the contents of transition metal compound as shown in Table 3.

(2) Production of Ceramics

By pressure moulding the raw material powder as before obtained, and then further hydrostatic compressing the obtained mouldings under pressure of 2 ton/cm², mouldings having the desired shape was obtained. The obtained mouldings was fired under atmospheric pressure at the given temperature as shown in Table 3. For reference, omitting the addition of the transition metal compounds, the raw materials wherein Y₂O₃ content is more than 3.0 mol.%, that is, using the unpreferable raw material characteristics of alumina powder and/or zirconia powder, the ceramic body was produced

(3) Characteristics of Raw Material Powder and The Ceramics made therefrom.

The following characteristics were measured on the raw material powder and the ceramics obtained above. The data measured on the characteristics are shown in Tables 1, 2 and 3.

(A) Size of partially stabilized zirconia particle and α -alumina particle:D

The size D can be calculated from the width at the half value of the peak of X ray diffraction by the following Schellar's formula:

$$D=0.9\lambda/\beta \cos\theta$$

λ : the wave length of X ray

β : the width at the half value of the diffraction peak

θ : the diffraction angle

(B) BET Specific surface area of partially stabilized zirconia particle and α -alumina particle
was measured by using micromeritics (machine manufactured by Shimazu Works).

(C) Breaking Toughness Strength of high density alumina zirconia ceramics: K_{Ic}
was measured by Vickers indent test.

The Vickers indenter was pressed to the polished surface of the samples, and the resulting indentation size and the resulting length of the generated crack were measured and K_{Ic} was calculated from the following formula which Niihara et al proposed.

The applied indentation load was 50 kgf.

$$(K_{Ic} \Phi / H a^{3/2}) (H/E\Phi)^{1/4} = 0.129 (c/a)^{-3/2}$$

Φ : restraint modulus(-3)

H: Vickers hardness

E: modulus of elasticity.

a: half value of diagonal length of indentation

c: length of crack generated from indentation.

(D) Bending strength of high density alumina zirconia ceramics:

was measured in accordance with JIS R 1601(1981) rule.

The sample of 3×4×40 mm in size was used, and measurement was carried out on span length of 30 mm under crosshead speed of 0.5 mm/min, and the value was determined by average from five samples.

(E) Content of tetragonal phase in the high density alumina zirconia ceramics

The surface of the sample was polished by diamond slurry containing 3 μ m in size of diamond particles, and then, X ray diffraction measurement was carried out on that surface followed by the calculation of the following formula.

$$\text{Tetragonal phase content (\%)} = \frac{(111)_t}{(111)_t + (111)_m + (111)_m} \times 100$$

(111)t:tetragonal (111) face diffraction intensity

(111)m:monoclinic (111) face diffraction intensity

(111)m:monoclinic (111) face diffraction intensity

(111)t diffraction peak includes cubic (111)c diffraction peak, but the calculation was carried out presuming that that peak is entirely by tetragonal diffraction.

(F) Grain size in the high density alumina zirconia ceramics.

The grain size was measured by observing the fracture face of the ceramics through scanning type electron microscope. It was confirmed that all samples except of reference samples have content of tetragonal phase of ZrO_2 in the resultant ceramics ranging more than 95 %. the grain size of ZrO_2 ranging 0.3 to 0.8 μm , and the content of Al_2O_3 ranging 1 to 2 μm .

5

EXAMPLE 2

Using acetate of transition metal, and methanol instead of ethanol, the procedures of Example 1 was repeated to obtain the raw material powder for the production of ceramic body, which contains transition metal compound. The resultant raw powder was shaped, calcined as in the procedure of Example 1, to yield the high density alumina zirconia ceramic body. The characteristics of the resultant ceramics were measured as in Example 1.

It was confirmed that all samples except of reference samples have content of tetragonal phase of ZrO_2 , in the resultant ceramics ranging more than 95 %, the grain size of ZrO_2 , ranging 0.5 to 1.0 μm , and the content of Al_2O_3 , ranging 1 to 3 μm .

Example 3

A given amount of α -alumina powder (grain size: 0.4 μ m, Specific surface area: 8 m^2/g) was added to an aqueous solution of ZrOCl_2 (or aqueous solution of ZrOCl_2 , containing a stabilizing agent) and agitated by ball milling to form uniform dispersion. The resultant dispersion was then added to excess ammonia water at such rate that the pH thereof was maintained at more than 9, and agitated, and then the resultant precipitation was filtered, washed with water, and dried to yield the combined deposit compound of alumina and zirconium compound.

Then, the resultant powder and nitrate of transition metal were dissolved in ethanol solution and put in a milling pot, and mixed, ground and then ethanol was evaporated to be dry so that the raw material powder was obtained for the production of the ceramic body. The resultant grain size of ZrO_2 in the combined powder was 200 \AA .

The resultant raw powder was shaped, and calcined as in the procedure, to yield the high density alumina zirconia ceramic body. The characteristics of the resultant were measured as in Example 1. The result of the measurement are shown in Table 3.

It was confirmed that all samples have content of tetragonal phase of ZrO_2 in the resultant ceramics ranging more than 95 %, the grain size of ZrO_2 ranging 0.5 to 1.0 μ m, and the content of Al_2O_3 ranging 1 to 3 μ m.

Table 1. Powder Characteristics of
Raw Zirconia 0236507

Species of Powder	Calcining Temp. (°C)	Amount of Y ₂ O ₃ (mol %)	Grain Size (Å)	Specific Surface Area (m ² /g)
Z - 1	800	0	150	30
Z - 2	900	1. 2	200	22
Z - 3	600	1. 7	120	42
Z - 4	950	2. 0	200	15
Z - 5	800	2. 5	150	32
Ref Z-6	1100	1. 7	350	5
Ref Z-7	900	5. 0	200	23

Table 2. Powder characteristics
of Raw Alumina

Species of Powder	Grain Size (μm)	Specific Sur- face Area (m ² /g)
A - 1	0. 6	7
A - 2	0. 6	6
A - 3	0. 1	30
A - 4	0. 4	8
Ref A-5	2. 0	2

Table 3. Sintering Condition and Characteristics of Ceramic Body (1)

No.	Raw Powder		Added Transition Metal		PSZ amount mol%	Sintering Temp. °C	Sintered Density g/cm ³	KIC MN/m ^{3/2}	Vickers Hardness kg/mm ²	Bending Strength kg/mm ²
	Al ₂ O ₃	ZrO ₂	Spec- cies	Amount mol%						
1-1	A-1	Z-1	Mn	0.3	10	1500	4.15	8.0	1650	80
1-2	"	Z-3	"	0.2	20	1450	4.32	8.5	1620	82
1-3	"	"	"	0.3	20	"	4.33	8.8	1600	90
1-4	"	"	Cu	0.3	10	1500	4.15	6.8	1630	77
1-5	"	"	"	0.3	20	1450	4.31	8.2	1630	85
1-6	A-2	Z-2	Zn	0.2	30	1400	4.51	10.2	1580	98
1-7	"	Z-3	Mn	0.2	10	1500	4.14	7.0	1700	82
1-8	"	"	"	0.3	10	1450	4.13	7.2	1670	80
1-9	"	"	Co	0.3	20	"	4.33	8.5	1610	89
1-10	A-1	Z-3	—	—	"	1500	4.00	5.2	1520	42
1-11	A-2	"	—	—	"	"	3.92	5.2	1500	530
1-12	"	MrZ-7	Mn	0.3	"	"	1.02	5.1	1520	503
1-13	A-1	MrZ-6	"	"	"	"	4.08	6.0	1540	590
1-14	MrA-5	Z-1	"	"	"	"	3.90	5.0	1480	10

Reference

0236507

Table 3. Sintering Condition and Characteristics of Ceramic Body (2)

No.	Raw Powder		Added Transition Metal		PSZ amount mol%	Sintering Temp. °C	Sintered density g/cm ³	KIC MN/m ^{3/2}	Vickers Hardness kg/mm ²	Bending Strength kg/mm ²
	Al ₂ O ₃	ZrO ₂	Spec. cies	Amount mol%						
2-1	A-3	Z-1	Mn	0.3	10	1450	4.16	7.0	1700	85
2-2	"	"	Co	0.2	10	"	4.15	7.2	1670	87
2-3	"	Z-3	Mn	0.2	20	"	4.33	8.3	1650	93
2-4	"	"	Ni	0.3	30	1400	4.51	9.2	1580	98
2-5	"	Z-5	Mn	0.3	40	1400	4.71	12.0	1550	102
2-6	"	"	Cu	0.3	20	1450	4.32	7.5	1620	85
2-7	A-4	Z-2	Fe	0.1	10	1500	4.15	8.0	1680	82
2-8	"	"	Zn	0.2	20	1450	4.33	8.5	1620	88
2-9	"	Z-3	Mn	0.3	10	1500	4.15	7.6	1690	78
2-10	"	"	Ni	0.2	20	1450	4.31	8.2	1630	88
2-11	"	"	"	0.3	30	1400	4.52	11.0	1570	92
2-12	"	Z-4	Co	0.3	40	"	4.70	12.0	1520	90
3-1	"	"	Mn	0.3	10	1450	4.16	8.2	1750	85
3-2	"	"	"	0.3	20	1400	4.33	8.6	1700	95
2-13	A-3	Z-3	"	"	20	1500	4.18	5.8	1530	60
2-14	A-4	"	"	"	20	"	4.20	5.8	1510	62
Reference										

The high density alumina zirconia ceramic body of the present invention is as shown in Examples, highly dense in sintered density, and has excellent breaking toughness value(K_{Ic}), and high bending strength and hardness.

In accordance with the present invention, a high density alumina zirconia ceramic body can be produced by using finely divided zirconia powder and a sinter-accelerating effect by transition metal compound(s). In the inventive ceramics, zirconia crystal is restrained to grow so that crystal phase of zirconia particle in the ceramics enables to maintain the tetragonal phase of zirconia in the ceramics even when the content of partially stabilized zirconia is increased, and even when the content of the stabilizing agent is reduced. Further, the crystal growth of alumina in the ceramics is suppressed.

By these two suppression of the crystal growth the resultant ceramic body is improved so that the breaking toughness value is increased to 12 MN/m². Further, the resultant ceramics has improved bending strength, and the improved hardness.

Therefore, the ceramic body of the present invention is expected to be used as a strong structural ceramic member such as abrasion resistant material, and mechanical member, and is useful in application such as cutting tool, and can be used for high performance material.

In view of the foregoing, the present invention provides alumina zirconia ceramics with high density, high strength, high hardness and excellent toughness, and a method of production thereof. Therefore, the present invention can provide industrial significance.

CLAIM

1. A high density alumina - zirconia ceramic body, the formulation of which comprises α -alumina ranging from 60 mole % to 99 mole %, zirconia containing more than 65 % of tetragonal phase content ranging from 1 mole % to 40 mole % and transition metal oxide(s) the atomic ratio of which to the combination of aluminium and zirconium ranges 0.01 % to 1 %
- 5
2. The ceramic body as claimed in claim 1, wherein the transition metal oxide is oxide(s) of at least one metal selected from the group consisting of Mn, Fe, Co, Ni, Cu and Zn.
- 10
3. The ceramic body as claimed in claim 1, wherein crystal size in average of Al_2O_3 is less than 3 μm .
- 15
4. The ceramic body as claimed in claim 1, wherein the average crystal size of ZrO_2 is less than 1 μm .
- 20
5. The ceramic body as claimed in claim 1, wherein zirconia is partially stabilized zirconia with Y_2O_3 .
- 25
6. The ceramic body as claimed in claim 1, wherein the content of Y_2O_3 in the partially stabilized zirconia is less than 3 mole %.
7. A process for the production of a high density alumina - zirconia ceramic body, the formulation of which comprises α -alumina ranging from 60 mole % to 99 mole %, zirconia containing more than 65 % of tetragonal phase content ranging from 1 mole % to 40 mole % and transition metal oxide(s) the atomic ratio of which to the combination of
- 30

aluminium and zirconium ranges 0.01 % to 1 %
which process comprising

0236507

removing solvent from the combined dispersion liquid comprising

- (a) α -alumina powder, or the precursor to generate α -alumina powder by heat decomposition,
- (b) zirconia powder, or the precursor to generate zirconia powder by heat decomposition and,
- (c) solution or suspension containing transition metal compound(s),

and drying the dispersion to produce powder material, if necessary, forming in a certain shape after heat decomposition, and sintering the material.

8. The process for the production of the ceramic body, as claimed in claim 7, wherein the crystal size of the partially stabilized zirconia powder is less than 300 \AA , BET specific surface area of the partially stabilized zirconia powder is more than $8 \text{ m}^2/\text{g}$, and the crystal size of α -alumina powder is less than $1.0 \mu\text{m}$, and the BET specific surface area is more than $5 \text{ m}^2/\text{g}$.

9. The process for the production of the ceramic body as claimed in claim 7, wherein the solution of the transition metal compound is mixed.

10. The process for the production of the ceramic body as claimed in claim 7, wherein alumina - zirconium combined powder produced by calcining the combined precipitation of alumina and zirconium compound, which is obtained from aqueous dispersion containing zirconium compound salt or zirconium salt and stabilizing agent therefor, alumina powder and precipitating agent is used as α -alumina powder and zirconia powder.

INTERNATIONAL SEARCH REPORT

0236507

International Application No. PCT/JP86/00449

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹⁾

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl ⁴ C04B35/10

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴⁾

Classification System	Classification Symbols
IPC	C04B35/10, 35/48

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵⁾III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁰⁾

Category ⁹⁾	Citation of Document, ¹⁰⁾ with indication, where appropriate, of the relevant passages ¹¹⁾	Relevant to Claim No. ¹⁰⁾
A	DE, B, 2549652 (Max-Planck-Gesellschaft zur Förderung Wissenschaften e.V.) 29 May 1980 (29. 05. 80) & US, A, 4298385 & JP, B2, 59-25748	1-10
A	DE, C, 2744700 (Feldmühle Aktiengesellschaft) 10 February 1983 (10. 02. 83) & US, A, 4218253 & JP, B2, 59-24751	1-10
A	DE, A, 3233019 (Max-Planck-Gesellschaft zur Förderung Wissenschaften e.V.) 8 March 1984 (08. 03. 84) & JP, A, 59-64567 & US, A, 4506024	1-10
A	JP, A, 59-190259 (Hitachi Metals, Ltd.) 29 October 1984 (29. 10. 84) (Family: none)	1-10

* Special categories of cited documents: ¹⁰⁾

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "8" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁾	Date of Mailing of this International Search Report ¹⁾
November 18, 1986 (18.11.86)	December 1, 1986 (01.12.86)
International Searching Authority ¹⁾ Japanese Patent Office	Signature of Authorized Officer ¹⁰⁾

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)